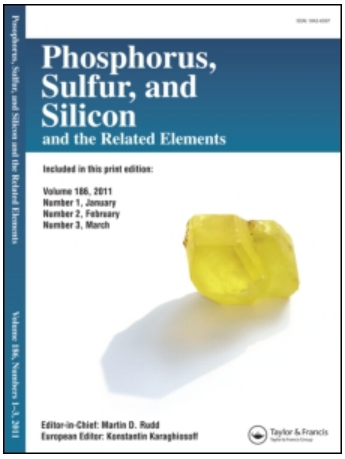

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HYDRO-DE-PHOSPHONIATION OF 4-SUBSTITUTED-4-TRIPHENYLPHOSPHONIO-S(4*H*)-OXAZOLONES WITH HYDROGEN IODIDE

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HYDRO-DE-PHOSPHONIATION OF 4-SUBSTITUTED-4-TRIPHENYLPHOSPHONIO-5(4*H*)-OXAZOLONES WITH HYDROGEN IODIDE

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4-Substituted-4-triphenylphosphonio-5(4*H*)-oxazolones, when reacted with hydrogen iodide in methylene chloride at room temperature, undergo hydro-de-phosphoniation to 5(4*H*)-oxazolonium salts, which react with methanol and triethylamine to give the corresponding N-acyl α-amino acid methyl esters. The possible mechanisms of hydro-de-phosphoniation is discussed.

Keywords: 4-Triphenylphosphonio-5(4*H*)-oxazolones; hydro-de-phosphoniation; reduction with hydrogen iodide; functionalization of glycine; 5(4*H*)-oxazolonium salts; mechanism

INTRODUCTION

Recently, we have described the effective synthesis of 4-phosphoranylidene-5(4*H*)-oxazolones (**1**) – a hardly known class of phosphorus ylides derived from 5(4*H*)-oxazolones[1]. We have also demonstrated that they display a reactivity pattern towards alkylating, acylating and halogenating agents similar to the reactivity of 5(4*H*)-oxazolone enolates[2–4]. In particular, we have developed simple and effective procedures for the alkylation of the ylides **1** that provide 4-C-alkylation products **2** (4-alkyl-4-triphenylphosphonio-5(4*H*)-oxazolones) in good yields. It should be stressed that an effective, direct, base-catalyzed 4-C-alkylation of 5(4*H*)-oxazolone enolates is possible only in the case of compounds with a bulky substituent

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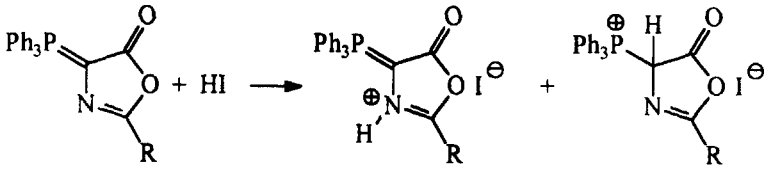
at position 4, as only this kind of 5(4*H*)-oxazolones is relatively little susceptible to competitive, base-catalyzed dimerization[2,5].

In the present paper we report the results of our investigations on the hydro-de-phosphoniation of phosphonium salts **2** with hydrogen iodide.

RESULTS AND DISCUSSION

Studying the reactivity of 4-phosphoranylidene-5(4*H*)-oxazolones towards Brønsted acids we stated, that the treatment of 4-triphenylphosphoranylidene-5(4*H*)-oxazolones **1a-b** with the equimolar amount of hydrogen iodide in methylene chloride results in the iminium salt protonated at the position 3 (ylide **1a**) or leads to a mixture of iminium and phosphonium salts protonated at the position 3 and 4, respectively (ylide **1b**)[4] (Scheme 1).

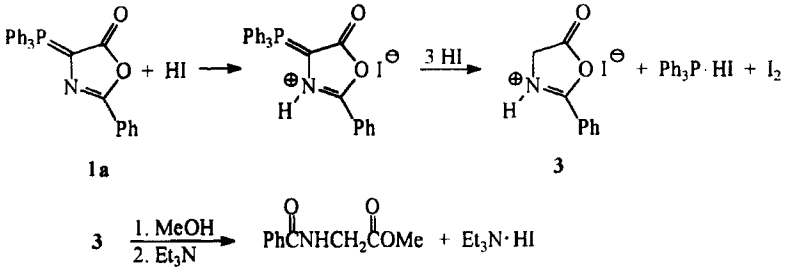


1a: R = Ph
1b: R = *t*-Bu

SCHEME 1

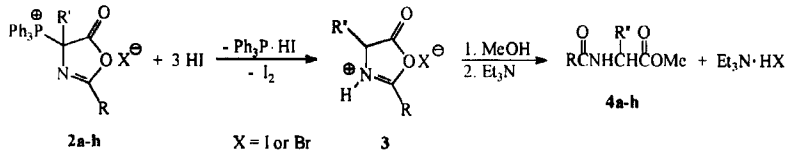
In a further experiment we have found that 2-phenyl-4-triphenylphosphonio-5(4*H*)-oxazolone **1a** treated with 3 moles of hydrogen iodide per 1 mole of the ylide was not transformed into the expected double protonated salt, but underwent hydro-de-phosphoniation to 2-phenyl-5(4*H*)-oxazolonium iodide **3** after a few minutes. Apart from this compound the reaction mixture contained also triphenylphosphonium iodide and iodine (Scheme 2).

2-Phenyl-5(4*H*)-oxazolonium iodide was identified based on its very characteristic IR spectrum (strong $\nu_{C=O}$ and $\nu_{C=N}$ bands at 1887 and 1651 cm^{-1}, respectively) as well as on ^1H and ^{13}C NMR spectra and the result of elemental analysis. A few 5(4*H*)-oxazolonium perchlorates with very similar IR spectra have been described by Boyd *et al.*[6] The reaction of the 2-phenyl-5(4*H*)-oxazolonium iodide with methyl alcohol, followed by making the reaction mixture alkaline with triethylamine, gave the expected methyl N-benzoylglycinate (**4a**) in an excellent yield.



SCHEME 2

The results of these experiments suggested that a similar hydro-de-phosphoniation under the influence of hydrogen iodide should be possible also in the case of 4-substituted-4-triphenylphosphonio-5(4*H*)-oxazolones **2.** Indeed, the treatment of salts **2b-g** with an excess of hydrogen iodide (3–5 mol of HI per 1 mol of the salt **2**) in methylene chloride at room temperature, followed by the treatment of the primary reaction product with methanol and triethylamine, gave the expected methyl esters of the corresponding N-acyl α-amino acids **4b-g,** usually in moderate to good yields; only in the case of the salt **2f** the yield was poor (Table I) (Scheme 3).



SCHEME 3

In the case of 4-bromo-2-phenyl-4-triphenylphosphonio-5(4*H*)-oxazolone bromide (**2a**) the debrominated glycine derivative **4a** was isolated as the only reaction product. Hydro-de-halogenation of α-halo carbonyl compounds under the influence of hydrogen iodide is a known reaction[7]. In the case of the salt **2h** instead of the α-methoxymethyl glycine derivative the α-iodomethyl derivative **4h** was obtained, probably as a result of the well-known cleavage of the C-O bond by hydrogen iodide[8]. The structure of the obtained methyl esters of N-acyl α-amino acids has been confirmed by their spectroscopic properties (IR, ^{1}H and ^{13}C NMR) as well as by satisfactory results of elemental analyses (see Tables I and II).

TABLE I Hydro-de-phosphoniation of 4-subtituted 4-triphenylphosphonio-5(4*H*)-oxazolones

Substrate				*Product*		*Time [h]*	*Temp. [°C]*	*2:HI molar ratio*	*Yield [%]*	*Mp [°C]*	*IR [cm^{-1}]*	*Elemental analyses (calcd./found) [%]*		
No.	*R*	*R'*	*X*	*No.*	*R''*							*C*	*H*	*N*
2a	Ph	Br	Br	**4a**	H	1	0	1:3	35	oil	3443w, 1750s, 1669s, 1523m, 1218m	59.40[a]/59.81	5.98[a]/5.84	6.93[a]/6.85
2b	Ph	Me	I	**4b**	Me	1.5	0	1:3	66	oil	3398w, 1742s, 1667s, 1522m, 1261m	63.76/63.45	6.32/6.23	6.76/6.37
2c	*t*-Bu	Me	I	**4c**	Me	15	20	1:3	80	oil	3440w, 1742s, 1663s, 1503m, 1200m	57.72/57.81	9.16/9.19	7.48/7.32
2d	*t*-Bu	CH_2Ph	Br	**4d**	CH_2Ph	70	20	1:3	56	90–92	3440w, 1740s, 1663s, 1503m, 1200m	68.42/68.08	8.04/8.04	5.32/5.28
2e	*t*-Bu	CH_2COOEt	I	**4e**	CH_2COOEt	1.5	0	1:3	65	oil	3450w, 1740s, 1665s, 1500m, 1205m	55.58/54.83	8.16/8.18	5.40/5.44
2f	*t*-Bu	CH_2COMe	I	**4f**	CH_2COMe	1.5	0	1:3	19	34–35	3450w, 1750s, 1663s, 1550m, 1210m	57.63/57.25	8.35/8.31	6.11/6.11
2g	*t*-Bu	CH_2Bt[b]	I	**4g**	CH_2Bt[b]	1.5	0	1:4	56	114.5–116	3438w, 1749s, 1667s, 1505m, 1200m	59.20/59.21	6.62/6.66	18.41/18.39
2h	Ph	CH_2OMe	I	**4h**	CH_2I	24	0	1:3	51	123–123.5	3445w, 1745s, 1674s, 1511m, 1210m	39.66/39.96	3.63/3.60	4.20/4.16
2h	Ph	CH_2OMe	I	**4h**	CH_2I	3	0	1:5	73	123–123.5				

[b]For the formula $C_{10}H_{11}NO_3 \cdot 0.5\ H_2O$; [b]Bt = benzotriazol-1-yl group.

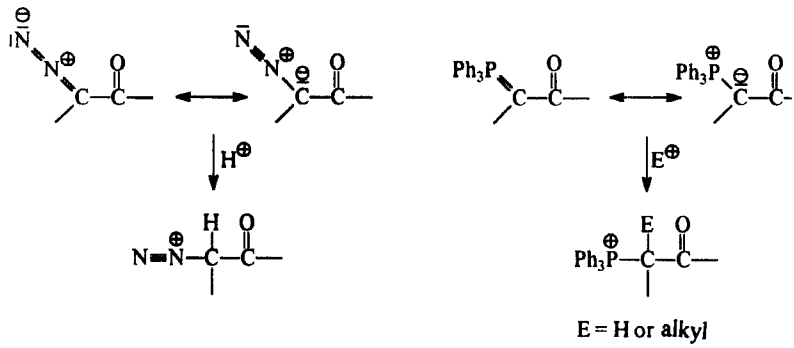
TABLE II ^{1}H and ^{13}C NMR spectral data of the obtained N-acyl α-amino acid methyl esters

Reaction product			*^{1}H-NMR ($CDCl_3$/TMS δ (ppm))*	*^{13}C NMR ($CDCl_3$/TMS δ (ppm))*				
No.	*R*	*R″*		$\overset{O}{\underset{C-NH}{}}$	$\overset{O}{\underset{C-O}{}}$	*NHCH*	*OMe*	*other carbons*
4a	Ph	H	7.86–7.78 (m, 2H, Ph); 7.58–7.42 (m, 3H, Ph); 6.69 (d, 1H, NH, J = 5.0 Hz); 4.26 (d, 2H, CH_2, J = 5.0 Hz); 3.80 (s, 3H, OMe)	170.6	167.6	41.7	52.5	133.6, 131.8, 128.6, 127.1 Ph
4b	Ph	Me	7.86–7.42 (m, 5H, Ph); 6.69 (d, 1H, NH, J_1 = 7.0 Hz); 4.82 (dq, 1H, CH, J_1 = 7.0 Hz, J_2 = 7.2 Hz); 3.8 (s, 3H, OMe); 1.53 (d, 3H, Me, J_2 = 7.2 Hz)	173.8	167.0	48.5	52.6	133.5, 131.8, 128.6, 127.1 Ph; 18.6 Me
4c	*t*-Bu	Me	6.21 (d, 1H, NH, J_1 = 7.2 Hz); 4.57 (dq, 1H, CH, J_1 = 7.2 Hz, J_2 = 7.2 Hz); 3.76 (s, 3H, OMe); 1.41 (d, 3H, Me, J_2 = 7.2 Hz); 1.22 (s, 9H, CMe_3)	178.0	173.9	47.9	52.4	38.6 CMe_3; 27.4 CMe_3; 18.4 Me
4d	*t*-Bu	CH_2Ph	7.38–7.05 (m, 5H, Ph); 6.05 (d, 1H, NH, J_1= 7.8 Hz); 4.82 (ddd, 1H, CH, J_1 = 7.8 Hz, J_2 = 5.7 Hz, J_3 = 5.7 Hz); 3.74 (s, 3H, OMe); 3.18 (dd, 1H, CH_2^a, J_2= 5.7 Hz, J_4 = 13.8 Hz); 3.09 (dd, 1H, CH_2^a, J_3 = 5.7 Hz, J_4 = 13.8 Hz) ; 1.15 (s, 9H, CMe_3)	177.8	172.3	52.3	52.8	135.9, 129.3, 128.5, 127.1 Ph; 37.7 CH_2; 38.7 CMe_3; 27.4 CMe_3
4e	*t*-Bu	CH_2COOEt	6.74 (d, 1H, NH, J_1 = 7.5 Hz); 4.84 (ddd, 1H, CH, J_1 = 7.5 Hz, J_2 = 4.5 Hz, J_3 = 4.5 Hz); 4.15 (q. 2H, CH_2, J_4 = 7.2 Hz) ; 3.76 (s, 3H, OMe); 3.02 (dd, 1H, CH_2^a, J_2 = 4.5 Hz, J_5= 17.0 Hz); 2.83 (dd, 1H, CH_2^a, J_3 = 4.5 Hz, J_5 = 17.0 Hz); 1.26 (t, 3H, Me, J_4 = 7.2 Hz); 1.22 (s, 9H, CMe_3)	177.2	170.5	47.5	51.6	170. 1 *C*OOEt, 59.9 O*C*H_2Me; 37.6 *C*Me_3; 35.1 *C*H_2CO; 26.3 C*Me*$_3$; 13.1 OCH_2*Me*

Reaction product			*^{1}H-NMR ($CDCl_3$/TMS δ (ppm))*	*^{13}C NMR ($CDCl_3$/TMS δ (ppm))*				
No.	*R*	*R″*		$\overset{\delta}{C}_{-NH}$	$\overset{\delta}{C}_{-O}$	*NHCH*	*OMe*	*other carbons*
4f	*t*-Bu	CH_2COMe	6.61 (d, 1H, NH, J_1 = 7.2 Hz); 4.66 (ddd, 1H, CH, J_1 = 7.2 Hz, J_2 = 4.2 Hz, J_3 = 4.2 Hz); 3.63 (s, 3H, OMe); 3.12 (dd, 1H, CH_2[a], J_2 = 4.2 Hz, J_4 = 18.3 Hz); 2.88 (dd, 1H, CH_2[a], J_3 = 4.2 Hz, J_4 = 18.3 Hz); 2.07 (s, 3H, Me); 1.05 (s, 9H, CMe_3)	177.2	170.7	47.1	51.6	206.0 *C*OMe; 43.7 *C*H_2CO; 37.6 *C*Me_3; 28.9 CO*Me*; 26.3 C*Me*$_3$
4g	*t*-Bu	CH_2Bt[b]	8.04 (d, 1H, Bt, H_4, J_1 = 8.4 Hz); 7.72–7.34 (m, 3H, Bt, H_5, H_6,H_7); 6.55 (d, 1H, NH, J_2 = 6.2 Hz); 5.16 (d, 2H, CH_2, J_3 = 4.4 Hz); 5.02 (dt, 1H, CH, J_2 = 6.2 Hz, J_3 = 4.4 Hz); 3.77 (s, 3H, OMe); 1.10 (s, 9H, CMe_3)	178.8	169.8	47.9	52.8	145.5, 132.0, 127.7, 124.2, 120.0, 109.4 Bt: C_{3a}, C_{7a}, C_6, C_5, C_4, C_7; 53.1 *C*H_2Bt; 38.7 *C*Me_3; 27.2 C*Me*$_3$
4h	Ph	CH_2I	7.86–7.45 (m, 5H, Ph); 6.96 (d, 1H, NH, J_1= 7.2 Hz); 4.99 (ddd, 1H, CH, J_1 = 7.2 Hz, J_2= 3.6 Hz, J_3= 3.6 Hz); 3.86 (s, 3H, OMe); 3.78 (dd, 1H, CH_2[a], J_2=3.6 Hz, J_4 = 10.2 Hz); 3.72 (dd, 1H, CH_2[a], J_3 =3.6 Hz, J_4 = 10.2 Hz)					

[a] One of the diastereotopic protons of the CH_2 group; [b] Bt = benzotriazol-1-yl group.

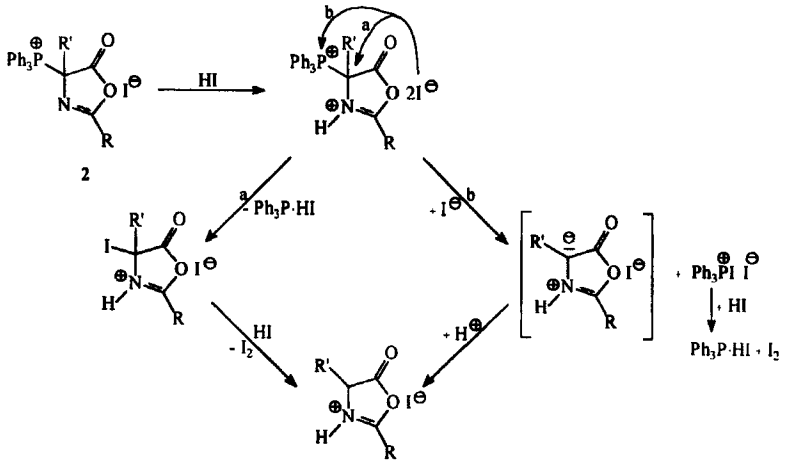
In the IR spectra of the investigated reaction mixtures we have observed two characteristic absorption bands at about 1890 and 1650 cm^{-1}, which correspond to 5(4*H*)-oxazolonium salts **3**; therefore, these salts may be considered to be primary hydro-de-phosphoniation products. The mechanism of hydro-de-phosphoniation of 4-triphenylphosphonio-5(4*H*)-oxazolones by hydrogen iodide is not quite evident. According to our best knowledge, the hydro-de-phosphoniation of phosphonium salt by hydrogen iodide has not been described in the literature. On the other hand, hydrogen iodide is well known as the reagent of choice for the reduction of α-diazoketones[9], which are, in some way, isoelectronic with 4-triphenylphosphoranylidene-5(4*H*)-oxazolones, whereas α-C-protonated α-diazoketones correspond to 4-C-protonated 4-triphenylphosphoranylidene-5(4*H*)-oxazolones or 4-substituted-4-triphenylphosphonio-5(4*H*)-oxazolones (Scheme 4).



SCHEME 4

According to Wolfrom and Brown[9] the reduction of α-diazoketones with hydrogen iodide consists in the α-C-protonation of α-diazoketone followed by the substitution of the diazo group by iodide anion. α-Iodoketone reacts in turn with hydrogen iodide to give the corresponding ketone as the product of hydro-de-iodination. An analogous mechanism of the hydro-de-phosphoniation of 4-triphenylphosphonio-5(4*H*)-oxazolones can be formulated as follows (Scheme 5, path "a"): The debromination of 4-bromo-2-phenyl-4-triphenylphosphonio-5(4*H*)-oxazolone bromide (**2a**) above mentioned supports this mechanism, (Scheme 5).

Another possible mechanism of the investigated reaction might consist in the attack of the iodide anion on the phosphorus (Scheme 5, path "b").



SCHEME 5

Recently, we have observed a similar hydro-de-phosphoniation of some phosphonium salts **2** under the influence of the methanol-DBU system, which evidently starts with the attack of a nucleophile (methanol or metanolate anion) on the phosphorus[10].

CONCLUDING REMARKS

The reported reaction, together with the previously described synthesis of ylides **1**[1] and the effective methods of their 4-C alkylation[2], offers a new way for the functionalization of the glycine α-position with alkylating agents.

EXPERIMENTAL

General

M. p.'s, determined in capillary tubes, are uncorrected. IR spectra were recorded on a Zeiss Specord M 80 spectrophotometer; the measurements

were carried out in CH_2Cl_2 (0.2 *M*) using cells of 0.075 mm. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian UNITY INOVA-300 spectrometer at operating frequencies of 300 and 75.5 MHz, respectively, in the FT mode using *TMS* as an internal standard.

Starting materials

A solution of HI in CH_2Cl_2 was prepared by saturating CH_2Cl_2 (25 ml) with a stream of dry HI (4–5 g) at 0°C. The obtained solution was diluted with CH_2Cl_2 (10 ml) and stored in a desiccator at about –5°C. Every time before the usage of this solution 1 ml of it was added to water (10 ml) and titrated with an aqueous solution of NaOH (0.1 M) in the presence of phenolphthalein. Gaseous, dry HI was obtained from tetralin (40 ml, 38.8 g, 0.29 mol) and iodine (8.7 g, 0.034 mol) according to the procedure given by Huber and Schmeisser[11]. Commercial grade acetonitrile and CH_2Cl_2 were distilled and dried over molecular sieves 4A. Ylides **1** and 4-substituted-4-triphenylphosphonio-5(4*H*)-oxazolones **2a-e** and **2h** were synthesized as previously described[1,2,4].

Synthesis of 4-acetylmethyl-2-t-butyl-4-triphenylphosphonio-5(4H)-oxazolone iodide 2f

Compound **2f** was prepared by heating the solution of ylide **1b** (1.00 g, 2.5 mmol) and iodoacetone (0.69 g, 3.75 mmol) in acetonitrile (2 ml) at 80°C for 13 hours, as described in our previous paper[4] (procedure B) to give **2f**, 1.18 g, 81%, mp. 165–165.5 °C. IR (cm^{-1}) 1821s, 1640s; ^1H NMR (δ): 7.98–7.78 (m, 15H, Ph_3P), 4.15 (dd, 1H, CH_2, $J_{H\text{-}H}$ = 18.3 Hz, $J_{H\text{-}P}$ = 5.7 Hz), 4.06 (dd, 1H, CH_2, $J_{H\text{-}H}$ = 18.4 Hz, $J_{H\text{-}P}$ = 5.8 Hz), 2.42 (s, 3H, Me), 0.97 (s, 9H, CMe_3); ^{13}C NMR [$\delta/J_{C\text{-}P}$ (Hz)] 201.7/13.4 (Me*C*O); 177.8/10.1, 173.4/3.5, 70.5/56.8 (oxazolone ring, C_2, C_5, C_4); 136.7/3.1, 135.3/9.8, 131.3/13.1, 113.2/84.2 (Ph_3P^+, C_4, C_2, C_3, C_1); 46.8 (CH_2); 34.6 (*C*Me_3): 30.8 (*Me*CO); 26.2 (C*Me*$_3$). Anal: Calcd. for $C_{28}H_{29}NO_3PI$: C, 57.45; H, 4.99; N, 2.39; P, 5.29 Found : C, 57.43; H, 5.03; N, 2.59; P, 5.07.

Synthesis of 4-(benzotriazol-1-ylmethyl)-2-t-butyl-4-triphenylphosphonio-5(4H)-oxazolone iodide 2g

A mixture of ylide **1b** (1.49 g, 3.7 mmol), 1-chloromethylbenzotriazole (0.503 g, 3.0 mmol), NaI (0.675 g, 4.5 mmol), and acetonitrile (3 ml),

placed in a sealed glass tube, was heated in an oil bath at 80°C for 5 hours. The reaction mixture was evaporated to dryness *in vacuo*. The residue was extracted three times with boiling benzene (5 ml) to remove unreacted ylide. The residue was dried again, dissolved in CH_2Cl_2 (3.5 ml), and the insoluble mixture of NaCl and NaI was filtered off. The filtrate was treated with diethyl ether (6 ml), the precipitated crystals were filtered, washed with a mixture of CH_2Cl_2 and diethyl ether in a ratio of 1:2 (*v/v*) and dried *in vacuo* (0.01–0.02 mmHg) at 45°C for 2 hours to give the pure product **2g**, 2.17 g, 89%, mp. 163–165 °C. IR (cm^{-1}): 1822s, 1642s: ^1H NMR (δ): 8.1–7.8 (m, 17H, Ph_3P and $C_4H_4N_3$, H_4, H_7), 7.58 (dd, 1H. $C_6H_4N_3$, H_6, J_1 = 7.2 Hz, J_2 = 7.5 Hz), 7.37 (dd, 1H, $C_6H_4N_3$, H_5, J_1 = 7.2 Hz, J_2= 7.8 Hz), 6.09 (dd, 1H, CH_2, $J_{H\text{-}H}$= 14.7 Hz, $J_{H\text{-}P}$ = 7.2 Hz), 5.96 (dd, 1H, CH_2, $J_{H\text{-}H}$ = 14.6 Hz, $J_{H\text{-}P}$ = 2.6 Hz), 0.52 (s, 9H, CMe_3); ^{13}C NMR [$\delta/J_{C\text{-}P}$ (Hz)]: 177.8/10.1, 171.9/3.4, 73.6/57.4 (oxazolone ring, C_2, C_5, C_4): 137.1/3.1, 135.2/10.4, 131.4/13.4, 112.6/85.1 (Ph_3P^+, C_4, C_2, C_3, C_1); 145.3, 133.8 128.8, 124.8, 119.7 ($C_6H_4N_3$, C_{3a}, C_{7a}, C_6, C_4, C_7); 50.5 (CH_2); 34.4 (CMe_3); 25.6 (CMe_3). Anal: Calcd. for $C_{32}H_{30}N_4O_2PI$: C, 58.19; H, 4.58; N, 8.48; P, 4.69 Found : C, 57.88; H, 4.64; N, 8.58, P, 4.50.

Reaction of 2-phenyl-4-triphenylphosphoranylidene-5(4H)-oxazolone 1a with HI. Synthesis of 2-phenyl-5(4H)-oxazolonium iodide (3)

To a stirred suspension of 2-phenyl-4-triphenylphosphoranylidene-5(4*H*)-oxazolone (0.842g, 2 mmol) in CH_2Cl_2 (2.9 ml) a solution of HI in CH_2Cl_2 (0.845 M, 7. 1 ml, 6 mmol) was added at 0°C. The reaction mixture was stirred at 0°C for 1 h, the precipitated pale-yellow crystals were separated by filtration, washed with CH_2Cl_2 and dryed *in vacuo* (0.02 mmHg) at 20°C for 1h to give the product **3**, 0.285 g, 49 %, mp 137.5–138.5 °C. IR (cm^{-1}): 1887s ($\nu_{C=O}$), 1651s ($\nu_{C=N}$); lit.[6] (for 2-phenyl-5(4*H*)-oxazolonium perchlorate in nujol mull): 1880 and 1662 cm^{-1}. Anal: Calcd. for $C_9H_8NO_2I$: C, 37.40 ; H, 2.79; N, 4.85. Found: C, 37.54; H, 2.73; N, 4.47.

Reaction of 2-phenyl-5(4H)-oxazolonium iodide (3) with MeOH

2-Phenyl-5(4*H*)-oxazolonium iodide (0.289 g, 1 mmol) and MeOH (2.25 ml, 1.78 g, 56 mmol) was stirred at room temperature for 0.5 h, and then Et_3N (0.2 ml, 0.15 g, 1.5 mmol) was added to make the solution slightly alkaline. The excess of MeOH was removed under reduced pressure, the product was isolated from the residue by column chromatography

on silica gel (Kieselgel 60 Merck, 0.063–0.200 mm, 25 ml) eluting with a mixture of benzene and ethyl acetate (1:1, *v/v*) to give methyl hippurate **4a** (0.189 g, 98 %). IR, ^1H and ^{13}C NMR spectral data as well as elemental analysis of the reaction product are given in Tables I and II.

Reaction of 4-triphenylphosphonio-5(4H)-oxazolones 2 with HI (General procedure)

To a stirred solution or suspension of 4-triphenylphosphonio-5(4*H*)-oxazolone (1 mmol) in some volume of CH_2Cl_2 such an amount of the solution of HI in CH_2Cl_2 (*ca.* 0.8–1 M) was added at 0°C, to achieve the molar ratio of **2** : HI as given in Table I, the total volume of the reaction mixture being *ca.* 10 ml. The reaction mixture was stirred at 0°C or at room temperature (*cf.* Table I) for a time as given in Table I, then the solvent was removed under reduced pressure. The residue was treated with MeOH (2.25 ml, 1.78 g, 56 mmol), the mixture was stirred for 0.5 h, and Et_3N (0.2–0.6 ml, 0.15–0.45 g, 1.5–4.5 mmol) was added to make the solution slightly alkaline. The mixture was worked-up as described above, using a mixture of ethyl acetate and benzene in a volume ratio of 1 :5 (**4a-b**), or 1:2 (**4c-h**) as an eluent for colum chromatography. Pure products were obtained after recrystallization of crude products from hexane or from a mixture of benzene and hexane.

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